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Theory for thermodynamic properties of molecular fluid mixtures

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Abstract . The effective pair potential for molecular fluid mixture of molecules possessing tetrahedral symmetry is expressed in the Lennard – Jones (12-6) form in terms of effective diameter $\sigma_{ab}^{T}(T_{ab}^{*})$ and well depth $\epsilon_{ab}^{T}(T_{ab}^{*})$ The theory is applied to calculate the thermodynamic properties of CH_4 and excess thermodynamic properties of binary mixtures such as Ar + CH_4 and CF_4+CH_4 In all these cases, the agreement is fairly good

Keywords Effective pair potential, excess thermodynamic properties, binary mixtures

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1. Introduction

Aim of the present paper is to estimate the thermodynamic properties of molecular fluid mixture. One of the theoretical approach for calculating the thermodynamic properties of (one component) molecular fluid is the 'preaveraged' potential method [1]. Recently, using the 'preaveraged' potential method [1], Karki *et al* [2] have derived the effective Lennard – Jones (ELJ) (12-6) potential to estimate the thermodynamic properties of simple molecular fluids such as N_2 and O_2.

In the present work, we extend this approach to derive the ELJ (12-6) potential for molecular fluid mixtures in the presence of octapole and hexadecapole moments. The ELJ (12-6) potential thus derived, is used to evaluate the thermodynamic properties of some molecular fluids and fluid mixtures.

2. Theoretical basis

We consider a molecular fluid mixture of nearly spherical molecules, which interact *via* the pair potential, given by

$$u_{ab}(r\omega_1\omega_1) = u_{ab}^{0}(r) + u_{ab}^{a}(r\omega_1\omega_2) \qquad (1)$$

where $r = |r_1 - r_1|$ and ω_i is the orientation of molecule i. Here, u_{ab}^{0} is a spherically symmetric potential (*i.e.* central potential) and u_{ab}^{a} is the angle-dependent part of pair potential. For central potential, we take the LJ(12-6) potential

$$u_{ab}^{0}(r) = 4\,\epsilon_{ab}\left[(\sigma_{ab}/r)^{12} - (\sigma_{ab}/r)^{6}\right], \qquad (2)$$

where ϵ_{ab} and σ_{ab} are, respectively, the well depth and molecular diameter of species a and b. For the angle dependent interaction potential, we take

$$u_{ab}^{a} = u_{ab}^{perm} + u_{ab}^{in} \qquad (3)$$

where u_{ab}^{perm} is the interaction between the permanent multipole moments of the species a and b and u_{ab}^{in} is the interaction of the induced multipole moments in one molecule with the permanent multipole moments in other molecules.

For a system of molecules, interacting *via* the pair potential given by eq. (1), we follow the method of Shukla *et al* [1] and obtain an expression for the orientation-independent 'preaveraged' pair potential in a compact form

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$$\Psi_{ab}(r) = 4\,\epsilon_{ab}\left(\left[\left\{(1-(30/7)\left((\alpha_a\phi_b^2+\alpha_b\phi_a^2)/\epsilon_{ab}\,\sigma_{ab}^{12}\right)\right\}\right.\right.$$

$$\times(\sigma_{ab}/r)^{12} - (264/175)\,\beta\,\epsilon_{ab}\left\{9\left((\Omega_a^2\Omega_b^2)/\right.\right.$$

$$\left.\epsilon_{ab}^2\,\sigma_{ab}^{14}\right)(\sigma_{ab}/r)^{14} + (65/2)\left((\Omega_a^2\,\phi_b^2\right.$$

$$\left.+\Omega_b^2\,\phi_a^2)/\epsilon_{ab}^2\,\sigma_{ab}^{16}\right)(\sigma_{ab}/r)^{16}$$

$$\left.+(13000/21)\left(\phi_a^2\phi_b^2\right)/\epsilon_{ab}^2\,\sigma_{ab}^{18}\right)(\sigma_{ab}/r)^{18}\Big\}\Big]$$

$$-\Big[(\sigma_{ab}/r)^6 + (3/8)\left(\left(\alpha_a Q_b^2+\alpha_b Q_a^2\right)/\epsilon_{ab}\,\sigma_{ab}^8\right)$$

$$\times(\sigma_{ab}/r)^8 + (6/5)\left(\left(\alpha_a\Omega_b^2+\alpha_b\Omega_a^2\right)/\epsilon_{ab}\,\sigma_{ab}^{10}\right)$$

$$\times(\sigma_{ab}/r)^{10} + (7/20)(\beta\epsilon_{ab})\left(Q_a^2Q_b^2/\epsilon_{ab}^2\,\sigma_{ab}^{10}\right)$$

$$\left.\times(\sigma_{ab}/r)^{10}\Big]\right). \tag{4}$$

Here, Q_a, Ω_a and ϕ_a are the quadrupole, octapole and hexadecapole moments, respectively, α_a is the polarizability of the molecule of species a and $\beta = (k\,T)^{-1}$ (T being the absolute temperature).

The 'preaveraged' pair potential Ψ_{ab} given by eq. (4) can be expressed in the form of the $LJ(12\text{-}6)$ potential by simply replacing $\sigma_{ab} \to \sigma_{ab}^T$ and $\epsilon_{ab} \to \epsilon_{ab}^T$. In order to obtain the expressions for σ_{ab}^T and ϵ_{ab}^T, we approximate $r/\sigma_{ab} \approx r_{min}/\sigma_{ab} \approx 2^{1/6}$ [3] and write eq. (4) as

$$\Psi_{ab}(r) = 4\,\epsilon_{ab}\left[(a_{ab}+\beta\epsilon_{ab}\,b_{ab})\,(\sigma_{ab}/r)^{12}\right.$$

$$\left.-\left(c_{ab}+\beta\,\epsilon_{ab}\,d_{ab}\right)(\sigma_{ab}/r)^6\right], \tag{5}$$

where

$$a_{ab} = 1-(30/7)\left(\left(\alpha_a\phi_b^2+\alpha_b\phi_a^2\right)/\epsilon_{ab}\,\sigma_{ab}^{12}\right), \tag{6}$$

$$b_{ab} = (264/175)\Big[(9/2^{13})\left(\left(\Omega_a^2\Omega_b^2\right)/\epsilon_{ab}^2\,\sigma_{ab}^{14}\right)$$

$$+(65/2^{2/3})\left(\left(\Omega_a^2\phi_b^2+\Omega_b^2\phi_a^2\right)/\epsilon_{ab}^2\,\epsilon_{ab}^{16}\right)$$

$$+(6500/21)\left(\phi_a^2\phi_b^2/\epsilon_{ab}^2\,\epsilon_{ab}^{18}\right)\Big], \tag{7}$$

$$c_{ab} = 1+\left(3/8(2^{2/3})\right)\left(\left(\alpha_a Q_b^2+\alpha_b Q_a^2\right)/\epsilon_{ab}\,\sigma_{ab}^8\right)$$

$$+\left(6/5(2^{2/3})\right)\left(\left(\alpha_a\Omega_b^2+\alpha_b\Omega_a^2\right)/\epsilon_{ab}\,\sigma_{ab}^{10}\right), \tag{8}$$

$$d_{ab} = \left(7/20(2^{2/3})\right)\left(Q_a^2\,Q_b^2/\epsilon_{ab}^2\,\epsilon_{ab}^{10}\right). \tag{9}$$

Eq. (5) can be expressed in the LJ (12–6) potential form

$$\Psi_{ab}(r) = 4\,\epsilon_{ab}^T\left[\left(\sigma_{ab}^T/r\right)^{12} - \left(\sigma_{ab}^T/r\right)^6\right], \tag{10}$$

where

$$\hat{\sigma}_{ab} \equiv \sigma_{ab}^T/\sigma_{ab} = F_{ab}^{-1/6}, \tag{11}$$

$$\hat{\epsilon}_{ab} \equiv \epsilon_{ab}^T/\epsilon_{ab} = (a_{ab}+\beta\,\epsilon_{ab}\,b_{ab})\,F_{ab}^2 \tag{12}$$

and

$$F_{ab} = (c_{ab}+\beta\,\epsilon_{ab}\,d_{ab})/(a_{ab}+\beta\,\epsilon_{ab}\,b_{ab}). \tag{13}$$

Thus, like one-component fluid [2], the effective pair potential of the molecular fluid mixture can be expressed as the ELJ (12-6) form in terms of σ_{ab}^T and ϵ_{ab}^T. Then the system can be treated as the LJ (12–6) fluid mixture. Thus, the molecular fluid mixture becomes equivalent to simple LJ (12-6) fluid mixture.

3. Thermodynamic properties of molecular fluid mixtures

We apply our theory to calculate the thermodynamic properties of molecular fluid mixtures. In our approach, we consider the reduced density $\rho_{ab}^* = \rho\sigma_{ab}^3$ and reduced temperature $T_{ab}^* = kT/\epsilon_{ab}$ and replace ρ_{ab}^* by $\rho_{ab}^{T^*} = \rho_{ab}^*\,\hat{\sigma}_{ab}^3$ and T_{ab}^* by $T_{ab}^{T^*} = T_{ab}^*/\hat{\epsilon}_{ab}$. Then the free energy and pressure of molecular fluid mixture are given by

$$A\left(\rho_{ab}^*, T_{ab}^*\right) = A_{LJ}\left(\rho_{ab}^{T^*}, T_{ab}^{T^*}\right), \tag{14}$$

$$P\left(\rho_{ab}^*, T_{ab}^*\right) = P_{LJ}\left(\rho_{ab}^{T^*}, T_{ab}^{T^*}\right), \tag{15}$$

where $A_{LJ}\left(\rho_{ab}^{T^*}, T_{ab}^{T^*}\right)$ and $P_{LJ}\left(\rho_{ab}^{T^*}, T_{ab}^{T^*}\right)$ are, respectively, the free energy and pressure of the LJ (12–6) fluid mixture at the reduced density $\rho_{ab}^{T^*}$ and reduced temperature $T_{ab}^{T^*}$.

4. One-component molecular fluids

We first apply our theory to study the thermodynamic behaviour of one-component fluids of molecules having tetrahedral symmetry like methane (CH_4). Such molecules have octapole and hexadecapole moments but not permanent moments of lower order.

The thermodynamic properties of a dense molecular fluid with the ELJ (12-6) potential, can be calculated using the Verlet – Weis [4] version of the Weeks – Chandler – Andersen (WCA) perturbation theory [5].

We employ this method to calculate the thermodynamic properties of molecular fluids. The calculated values of the configurational internal energy U and pressure for fluid CH_4 are

ɔmpared with the experimental data [6, 7] in Table 1. The ɪreement is found to be good.

ıble 1. Configurational internal energy βU/N and pressure P of fluid

K)	ρ (mol-l^{-1})	-βU/N		P(atom)	
		Present	Expt.[6,7]	Present	Expt.[6,7]
10	16 20	2.213	2.073	203.46	200
	18 56	2.415	2 367	304 25	300
	21 02	2.761	2 708	507.68	500
	24 16	2.896	3.080	1010 17	1000
10	13 83	2.146	1 681	101 23	100
	18 52	2 578	2 588	204 28	200
	22 26	3 224	3 143	508 75	500
	25.03	3.503	3 543	1025.65	1000

Thermodynamic properties of binary mixtures

In this section, we apply our theory to estimate the ıermodynamic properties of a binary mixture of molecules of ɔecies 1 and 2. The unlike force parameter σ_{12} and ϵ_{12} of the ɔecies 1 and 2 are given by the following combination rules

$$\sigma_{12}^T = \left(\sigma_{11}^T + \sigma_{22}^T\right)/2, \tag{16a}$$

$$\epsilon_{12}^T = \xi_{12}\left(\epsilon_{11}^T\ \epsilon_{22}^T\right)^{1/2}, \tag{16b}$$

here ξ_{12} is an adjustable parameter, which is less than unity. Ve have used the values of ξ_{12} reported by Henderson and conard [8].

We adopt the van der Waals one (vdW1) fluid theory of ıixture [9] to calculate the properties of the effective LJ fluid ıixture. This theory approximates the properties of a mixture by ıose of a fictitious pure fluid with the interaction parameters

$$\sigma_1^{T^1} = \sum_{a,b} x_a\ x_b\ \sigma_{ab}^t, \tag{17a}$$

$$\epsilon_1^T\ \sigma_1^{T^1} = \sum_{a,b} x_a\ x_b\ \epsilon_{ab}^T\ \sigma_{ab}^{T^1}, \tag{17b}$$

/here σ_{ab}^T and ϵ_{ab}^T are the force parameters of the effective LJ 12-6) potential of mixture of species a and b. Here, $x_a = N_a / N$ ı the concentration of species a.

In the vdW fluid theory of mixture, the free energy, enthalpy nd pressure of the effective LJ(12-16) fluid mixture are given by

$$A_{LJ} = A_x + NkT \sum_a x_a \ln x_a + \text{second order term}, \tag{18}$$

$$H_{LJ} = H_x + \text{second order term}, \tag{19}$$

$$P_{LJ} = P_x + \text{second order term}, \tag{20}$$

where A_x, H_x and P_x are the values of the free energy, enthalpy and pressure for the pure fluid containing N molecules in volume V and Temperature T, with molecules interacting *via* the effective LJ (12-6) potential with the parameters σ_x^T and ϵ_x^T.

In this paper, we calculate the excess thermodynamic properties at zero pressure. One can use expressions due to Grundke *et al* [10] to evaluate A_x, H_x and V_x at $P = 0$. Then, the excess Gibbs function G^E, excess enthalpy H^E and excess molar volume V^E are given as

$$G^E = G_X - x_1\ G_1 - x_2\ G_2\ , \tag{21}$$

$$H^E = H_x - x_1\ H_1 - x_2\ H_2\ , \tag{22}$$

$$V^E = V_x - x_1 V_1 - x_2 V_2\ . \tag{23}$$

These excess thermodynamic properties are demonstrated for Ar + CH_4 at T=91.0 K and CF_4 + CH_4 at T = 111.0 K for P = 0 and $x_1 = x_2 = 0.5$ in Table 2 along with the experimental data [8]. The agreement is good for the CF_4 + CH_4 mixture. However, in the case of Ar + CH_4, the agreement is not so good.

Table 2. Excess thermodynamic properties of the binary mixtures at P = 0 and $x_1 = x_2 = 0.5$

System	T(K)		G^E (J-mol^{-1})	H^E (J mol^{-1})	V^E (cm^3-mol^{-1})
Ar+CH_4	91	Present work	102	133	0 31
		(Expt [8]	74	103	0 17
CF_4 + CH_4	111	Present work	345	485 5	1 26
		Expt [8]	360		0 88

6. Concluding remarks

We have extended the theory developed earlier for one – component molecular fluid to the molecular fluid mixture. The effective pair potential is expressed in the LJ (12-6) form by simply replacing $\sigma_{ab} \rightarrow \sigma_{ab}^T$ and $\epsilon_{ab} \rightarrow \epsilon_{ab}^T$. This approach simplifies the problem of estimating the excess thermodynamic properties of molecular fluid mixtures of molecules possessing tetrahedral symmetry in terms of those of the spherically symmetric fluid mixture. We apply our theory to some cases, where the agreement is found to be good.

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